Background levels of heavy metals in surficial sediments of the Gulf of Lions (NW Mediterranean): An approach based on ^{133}Cs normalization and lead isotope measurements

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Among several potential normalizers, stable Cs (^{133}Cs) depicted the best ability to correct for the grain-size effect of shelf sediments and was used to estimate regional background levels of heavy metals.

Abstract

This paper presents an attempt to reach natural background levels of heavy metals in surficial sediments of the Gulf of Lions (NW Mediterranean). To correct for the grain-size effect, normalization procedures based on a clay mineral indicator element are commonly used, after a first grain size separation by sieving. In our study, we tested the applicability of this method with respect to commonly used normalizer elements, and found that stable Cs shows the best ability to reflect the fine sediment fraction. Background levels were successfully reached for Co, Cr, Cu, Ni and Pb, compared to various literature references. Nevertheless, in the case of lead, the normalized data depicted a general enrichment in all samples, and the natural levels could only be reached when concentrations were corrected for the atmospheric contribution by analysing lead isotope ratios. Also for Zn, a general enrichment was found in our samples, although less important.

1. Introduction

The first step when analysing the spatial distribution of the heavy-metal pollution in marine sediments is to account for the often considerable variability of natural concentrations that can be related to the variations of grain-size distribution and the mineralogical composition of the samples. It is commonly admitted that elements like metals show a strong affinity with the clay fraction and its coating formations (e.g. organic matter,

iron and manganese oxides). From one site to another, the grain-size distribution is rarely homogeneous and greater concentrations of elements do not automatically reflect anthropogenic inputs, but may also be due to a greater clay mineral content or to the abundance of minerals that are naturally enriched in the considered metal (Angelidis and Aloupi, 2001). Based on the metal concentrations alone, it is therefore difficult to distinguish between anthropogenic and natural sources.

For these reasons, various normalization procedures have been proposed. As a result, the normalized concentrations of equally polluted samples, but with different grain-size distributions, should not differ significantly (Kersten and Smedes, 2002). The separation of

the clay fraction ($<$2 μm) and the successive analysis of the metal content in this fraction alone would be the ideal normalization procedure. But the process is laborious and for practical reasons, the $<$63 μm fraction (clays+silts) is commonly separated. Unfortunately, such method does not avoid the considerable variability of the mineralogical composition and of the clay content between two areas. Based on the results of recent intercomparison exercises, Kersten and Smedes (2002) therefore recommend a two-tiered normalization approach including both sieving ($<$63 μm) and geochemical correction. This last consists of dividing the measured metal concentrations by the concentrations of certain elements which are considered to be proxies of the clay content (e.g. Al, Fe).

There are no clear rules established for the choice of the normalizer element, although this step is naturally of great importance because the distribution of the normalization element may also be variable in space. Several quality criteria have been defined (Luoma, 1990): first, the normalizer must covary in proportion with the natural concentrations of the metals of interest. Second, it must be insensitive to anthropogenic sources, and finally, it should not be influenced by changes in the geochemical conditions such as variations of the redox potential. Nevertheless, the choice of the normalizer element still remains somewhat subjective and often varies from one study to another. This makes it difficult to compare the values between different geographic and physiographic areas.

The purpose of our work was to test the power of different normalizer elements to detect natural background levels, and to identify an enhancement of the values due to pollution. The metals we investigated were Co, Cr, Cu, Ni, Pb and Zn, whereas the potential normalizer elements we tested were Al, Fe, Sc, Cs and Co. Sediment samples were taken as surface sediments from the Gulf of Lions in the NW Mediterranean, spreading over the entire platform and the submarine canyons down to a water depth of 1100 m. Our choice of the normalizer element that is the most suitable for tracking pollution in the sediments is based (i) on its degree of correlation with the fine fractions in the samples, (ii) on the degree of detail that can be obtained in the reconstruction of the spatial distribution patterns of polluted and unpolluted samples, and (iii) on their capability to produce natural background levels that are in agreement with other literature sources.

2. Material and methods

2.1. Sampling area and geochemical analyses

The Gulf of Lions is one of the largest continental platforms in the Mediterranean Sea, which receives various sources of particulate matter, both of riverine and atmospheric origins. By far the major part of the terrestrial input originates from the Rhône River, accounting for about 80% of the overall riverine input to the Gulf of Lions (Durrieu de Madron et al., 2000). Other sources of terrestrial particles are the relatively small coastal rivers, which show a highly variable discharge regime and for which the average sediment discharge is much more difficult to estimate (e.g., the Têt, Aude, and Hérault rivers; see Fig. 1). Industrial activity in the Rhône river basin is also clearly more elevated than in the smaller river basins in the Western part of the Gulf of Lions, indicating that most of the riverine metal pollution should be introduced by this river.

The platform sediments in the Gulf of Lions follow a granulometric gradient from the coastline to the outer shelf, as this has been described by Aloisi et al. (1973) in a high resolution sampling study. This gradient consists of a sandy band with silty sedimentary units in front of the river mouths (the so-called prodeltas), followed by a middle-shelf mudbank, and finally by a mix of relic sands and modern fine-grained sediments near the canyon heads.

The sediment samples analysed in this study were collected during an oceanographic cruise in November 2002 at 51 stations in the entire Gulf of Lions (Fig. 1) using a Multicorer or box corer. Organized by the Institut de Radioprotection et de Sécurité Nucléaire (IRSN) group, this campaign (REMORA 3) was devoted to a radionuclide and trace metal contamination assessment in the entire Gulf of Lions.

At each point, a sediment core was sub-sampled with an acid pre-cleaned PVC tube. The surficial sediments were collected as the first 0.5 cm of the cores. Samples were stored in plastic bags and immediately deep-frozen on board (-15 °C). On return to the laboratory, they were lyophilized.

Granulometric analyse were performed using a laser granulometer Sequoia LISST-100 ($n=46$). Lyophilised samples were first diluted in Milli-Q water and then passed into a sonification bath for 20 s to eliminate aggregates. Duplicates were realized on each sample to test the reproducibility of the procedure and the results were averaged. The instrument distinguishes the contribution of the different particle diameter classes, ranging from 1.5 to 230 μm. As trace and major elements were analysed in the $<$63 μm fraction, we only focused on the grain size distribution in this fraction.

Sediment samples for major and trace element determinations were lightly ground in a mortar to break up aggregates and then dry sieved ($<$63 μm), using an acid pre-cleaned nylon mesh. The fine fraction was totally digested by concentrated HF, HNO_3 and $HClO_4$ acids to dryness on a hot plate. The residue was solubilized by HNO_3 and diluted to volume. The resulting solution was
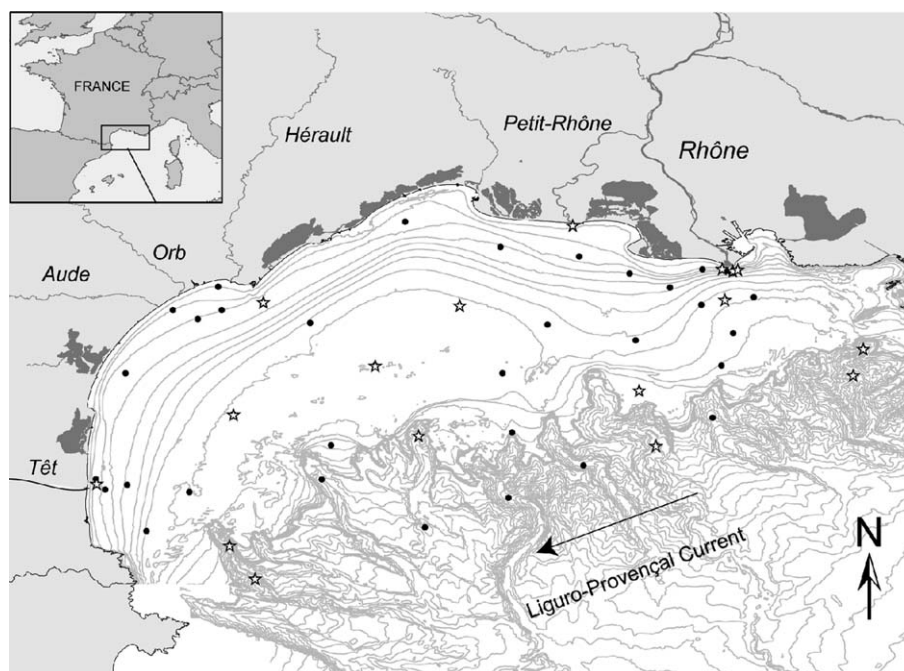
Fig. 1. Study area and sampling stations (black points and open stars). Stars refer to samples analysed for lead isotopic composition. The bathymetry has been kindly supplied by S. Berné, IFREMER (Brest).

then analysed for trace metals ($n=49$) and stable lead isotopes ($n=17$) by a Perkin-Elmer ELAN 6000 ICP-MS at the Laboratoire des Mécanismes de Transfert en Géologie (Toulouse, France). Major element analyses were performed by ICP-AES ($n=47$) at the Centre Européen de Recherche et d'Enseignement en Géosciences (Aix-Marseille, France). The different steps, from sieving to chemical analyses, occurred in clean rooms.

Accuracy was controlled by the use of numerous certified standards, e.g. the MESS-2 and GSMS-3 marine sediments for trace metal determination (see Table 1) and the NIST SRM-981 standard for lead isotopic analyses (not shown).

2.2. Statistical determination of the background levels

Based on the assumption that natural metal concentrations should depict a high degree of correlation with the normalizer element, regional background concentrations can be estimated by linear regression of the normalizer against the natural metal concentrations. Ideally, in unpolluted areas, the natural concentration ranges should be reached, whereas in polluted areas, the values should plot significantly above the regression line. To reach the natural range of the metals, samples suspected to receive any anthropogenic input must hence be removed from regression.

For each of the studied metals, we therefore performed linear regressions with the different normalizer elements, after log-transformations of all data in order to satisfy the assumption of constant variance and normality (Schropp and Windom, 1988). A 95% prediction interval has been drawn for each regression using standard statistical software. Then, all samples that were standing outside the upper limit were eliminated and considered as enhanced (Doherty et al., 2000). After each elimination step the regression was recalculated. This process was repeated until no sample fell outside the upper limit. Fig. 2 shows some examples of this procedure when using Cs as normalizer element.

Even if the number of the excluded samples varies from one regression to another, one can generalize that by far most of the enhanced samples referred to the same zones in the Gulf of Lions. They correspond on the one hand to the prodeltas of the major rivers (e.g. the Rhône,

Table 1
Control of analytical accuracy based on the use of MESS-2 and GSMS-3 marine sediment standards. Concentrations are in ppm

Element	MESS-2	Measured	Recovery (%)	GSMS-3	Measured	Recovery (%)
Co	13.8	14.3	103.6	53	55.7	105.1
Cr	106	106.8	100.8	38	36.4	95.8
Cu	39.3	39.0	99.3	231	242.0	104.8
Ni	49.3	48.9	99.2	108	107.7	99.7
Zn	172	172.3	100.2	142	150.2	105.8
Pb	21.9	23.2	106.0	22	21.2	96.4
Cs	–	–	–	4.5	4.5	100.0
Sc	–	–	–	15	14.6	97.3
Al_2O_3	–	–	–	77000	74390	96.6
Fe_2O_3	–	–	–	38100	36930	96.9

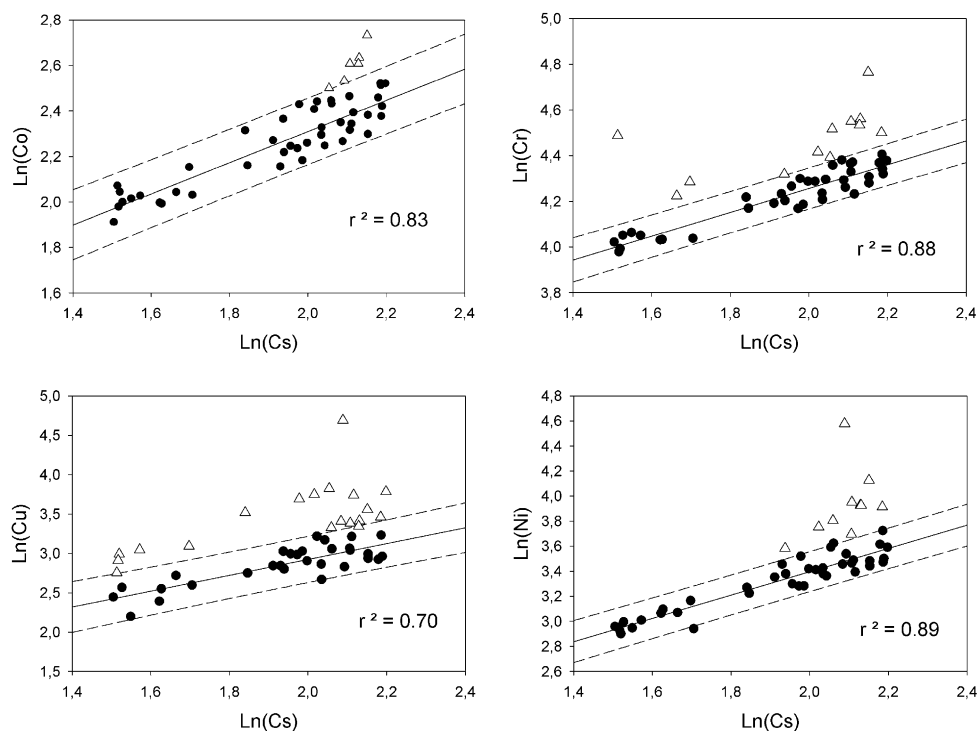Fig. 2. Determination of natural background values for Co, Cr, Cu and Ni based on their correlation with Cs ($n=49$). The upper triangles are the samples which have been successively removed from the regressions (see text). Values were log-transformed. The dotted lines represent prediction interval at the 95% confidence level.

Aude and Têt rivers) and on the other hand to a zone in the south part of the Gulf, stretching along the canyon heads. According to the general circulation scheme (Millot, 1990), it is here where most of the particles entering the Gulf via the Rhône River are supposed to be exported from the platform to the open marine system. To illustrate this general picture, Fig. 3 summarises the location of the enhanced stations according to the statistical analysis of Co, Cr, Cu and Ni content.

The technique described above is a frequently applied procedure for the determination of natural background levels in marine sediments. An alternative solution consists of measuring the metal concentrations in the deepest samples of sediment cores (Veinott et al., 2001; Leivuori, 1998), based on the hypothesis that early diagenetic processes did not alter the vertical distribution of the considered elements. Marin (1998) investigated the heavy metal content in several sediment cores in the Gulf of Lions and we therefore also compared our results with those of pre-anthropogenic samples in this study.

3. Results and discussion

3.1. Choice of the normalizer element

Various elements have been proposed in the literature to be clay mineral indicators and hence potential normalizers. Some of them are Al, Fe, Li, Sc, stable Cs and Co. Among these elements, Al and Fe have been the most frequently used in estuarine and coastal studies (Din, 1992; Tam and Yao, 1998; Schiff and Weisberg, 1999), while Li, Sc and Cs are more exotic and were used to a lesser extent. Li has been proposed as an alternative for Al in high latitude areas (Loring, 1990). Sc, with the difficulty of its determination because of its close association with Fe hydroxides (Loring, 1991), has been used in rare cases; a previous study in the Gulf of Lions referred to this element for the normalization of sediment data (Grousset et al., 1995).

Caesium, structurally combined in clay minerals (Loring, 1991), was revealed by Ackermann (1980) to be suitable for use in estuarine and coastal sediments, although it is only rarely used in the literature for metal data normalization. In a comparative study, the latter author demonstrated the high dependence of the Cs concentration in the total sediment on the percentage of the fraction $<20\mu m$, the phase highly associated with metals, indicating that Cs is a good fine-grained sediment indicator. Also cobalt, associated with silicate and clay minerals (Förstner and Wittmann, 1981) has recently been reported as a useful normalizer (Matthai and Birch, 2001). Li was not analysed in our study, so we did not test the normalization capacity of this element.

All of the normalizer elements discussed above have in common that they are normally well correlated with
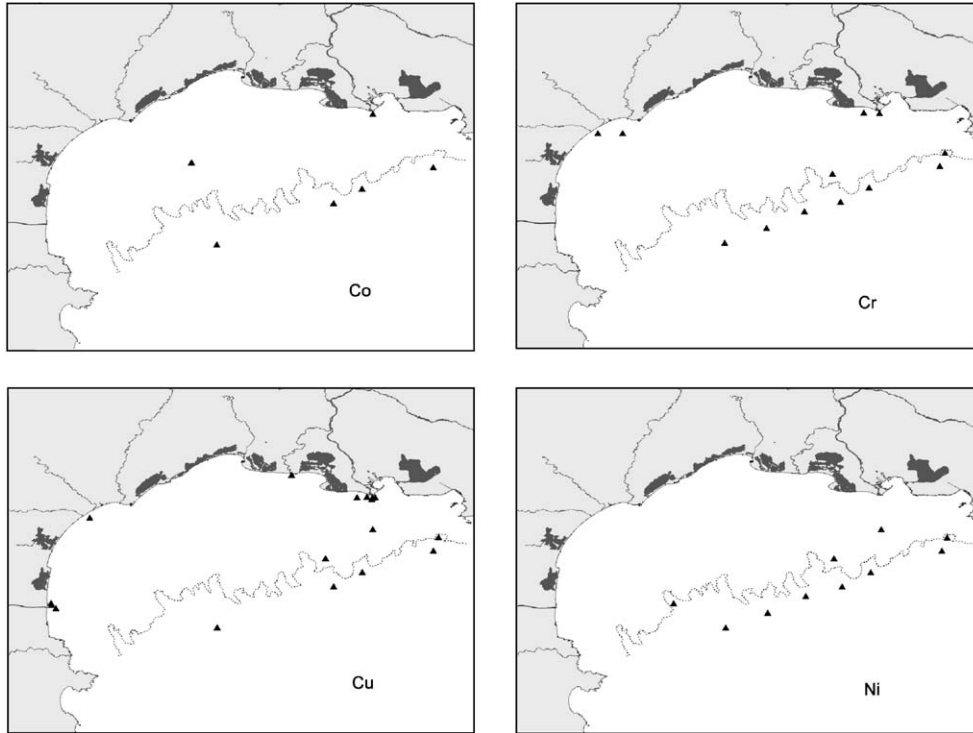
Fig. 3. Geographic locations of samples revealing enhanced contents of Co, Cr, Cu and Ni. For additional information, the boundary of the shelf has been represented, showing the complexity of the canyon heads distribution.

the clay content ($<2\mu$m) in the samples. This is also the case in our study (Fig. 4 and Table 2). Table 2 presents the affinities of the potential normalizers with the studied metals (before and after the statistical removal of enhanced samples) and clay fraction. For additional information, we presented the correlations with the fraction <20 μm, also considered as a high metal-bearing phase (Ackermann, 1980). All coefficients are positive and significant, except for Cu versus the clay content.

According to our results, Cs depicts the highest correlation coefficients, both with the fine fractions (less than 2 and 20 μm fractions, $r^2 = 0.82$ and 0.92, respectively, $n = 46$) and with the heavy metals

investigated, compared to the other candidates. This indicates that this element is the most suitable normalizer element in the Gulf of Lions. Moreover, the number of samples that were removed from the regressions due to an enhancement of the values is significantly higher than for the other potential normalizers, suggesting that Cs presents greater potential for the detection of enriched samples. For the other normalizer elements, the detection of outliers may be more difficult because of the generally weaker correlations, whipping out the differences between the natural and the slightly enhanced values.

The better ability of Cs to trace the clay content in the samples is also confirmed when looking at the variability
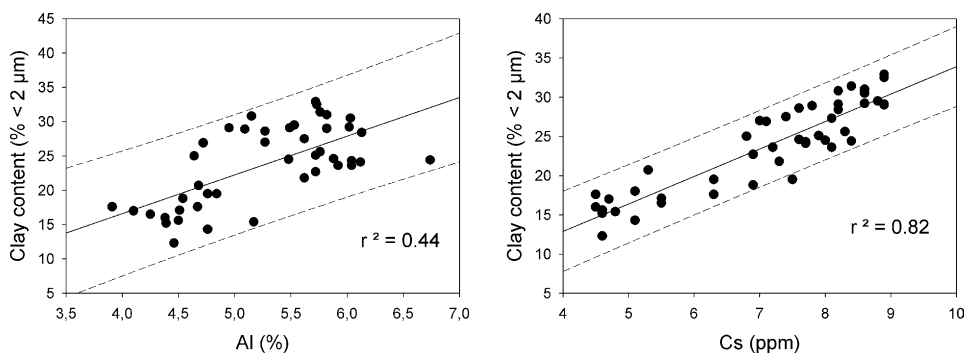

Fig. 4. Relationships between clay content (% <2 μm) and Al (%) and Cs (ppm) ($n = 46$), respectively. The dotted lines represent prediction interval at the 95% confidence level.

Table 2
Correlation coefficients (r^2) between various elements analysed in this study, as well as between these elements and fine fractions in the samples (<2 and 20 μm content)

Element	Al	Fe	Sc	Cs	Co	<2 μm	<20 μm
< 2 μm	0.44	0.44	0.30	0.82	0.60	—	0.84
< 20 μm	0.62	0.59	0.39	0.92	0.59	0.84	—
Co	0.49/0.53* (3)	0.64/0.67* (1)	0.49 (0)	0.76/0.83* (6)	—	0.60	0.59
Cr	0.25/0.54* (7)	0.48/0.57* (5)	0.48 (0)	0.48/0.88* (12)	0.74/0.87* (5)	0.58	0.57
Cu	0.18/0.30* (6)	0.21/0.42* (5)	0.32/0.56* (6)	0.28/0.70* (19)	0.31/0.58* (6)	0.07	0.11
Ni	0.46/0.62* (6)	0.53/0.69* (4)	0.39/0.46* (1)	0.61/0.89* (10)	0.67/0.91* (2)	0.44	0.42
Pb	0.38/0.52* (5)	0.49/0.68* (4)	0.51/0.55* (2)	0.67/0.81* (6)	0.67/0.73* (1)	0.43	0.5
Zn	0.24/0.41* (6)	0.32/0.54* (6)	0.35/0.72* (7)	0.35/0.80* (11)	0.31/0.43* (5)	0.12	0.22

Values were log-transformed, with the exception of granulometric percentages ($n=47$ for major elements; $n=49$ for trace metals; $n=46$ for 2 and 20 μm fractions). *Correlation coefficient after the removal of enhanced samples. (x) number of enhanced samples removed from the regressions.

of the ratios of the different normalizer elements over the clay fraction in the Gulf of Lions. For all elements, one finds a general trend of decreasing ratios from the coastline to the middle-shelf mudbank, which means from silty sand-rich to clay-rich sediments. It is therefore possible that these trends can be attributed to the non-clay component in the samples, which also may influence the measured normalizer concentrations in the <63 μm fraction. Nevertheless, it has to be pointed out that Cs appears to be clearly less sensitive to this variability in the study area compared to the other elements. Considering all samples, the standard deviation of this ratio is only about 11% of the mean value for Cs, compared to 20% for Al, 21% for Fe, 24% for Sc and 16% for Co (Table 3).

In this context it is also interesting to note that speciation analyses of trace metals in local fine-grained sediments (<63 μm) via sequential extractions (Marin, 1997, 1998) revealed that 98% of the total Cs is included in the residual fraction, compared to 93% for Al, 90% for Fe and 80% for Sc. This confirms the detrital origin of Cs and its structural link with the fine particles, which is a necessary condition for the geochemical tracing of these particles in the marine environment.

As a result, Cs will be considered in the following as the most suitable element for the normalization procedure. Also Co may be an alternative choice, since this element has a similar behaviour to Cs in our samples (although the correlations are slightly weaker).

3.2. Natural background levels

Our method to distinguish between natural and anthropogenic enhanced metal content is naturally somewhat arbitrary, which means that the so determined natural background values have to be considered with caution. The regression approach we applied is only valid when non-polluted samples co-exist together with polluted ones in the investigated area. When pollution affects almost all of the samples, e.g. by a widespread introduction of the pollutants of atmospheric origin, our method should lead in "natural" levels that are too elevated compared to the real background values.

We therefore compared our background levels based on the Cs normalization with the corresponding ratios in commonly cited reference values taken from the literature (Table 4). These values correspond to the terrigenous shales of Taylor and McLennan (1985) and of Krauskopf (1967), as well as to the average composition of the suspended particles in the Parana (Depetris et al., 2003) and the Amazon Rivers (Gaillardet et al., 1997). In addition, the corresponding ratios of sediments from local cores (pre-anthropogenic levels) of Marin (1998)

Table 4
Natural metal/Cs ratios from different sources

Sources	Co/Cs	Cr/Cs	Cu/Cs	Ni/Cs	Pb/Cs	Zn/Cs
This work (mean ratios)	1.4	9.9	2.51	4.06	5.27/2.20[a]	13.45
Standard deviation	0.14	1.22	0.38	0.31	0.55/0.41[a]	1.51
Parana river particles[b]	1.6	6.6	5	3.3	2.5	—
Amazon river particles[c]	1.45	8.55	—	3.25	2	—
Shale 1[d]	1.53	7.33	3.33	3.67	1.33	5.67
Shale 2[e]	4	20	11.4	19	4	16
Local Deep sediment[f] ($n=3$)	1.34	9.76	2.67	5.80	2.28	8.49
Standard deviation	0.11	1.05	0.67	1.64	0.26	0.61

[a] Without atmospheric contribution.
[b] Depetris et al. (2003).
[c] Gaillardet et al. (1997).
[d] Taylor and McLennan (1985).
[e] Krauskopf (1967).
[f] Marin (1998).

Table 3
Variability of the normalizer/clay ratios in the study area

Ratios	Al/clays	Fe/clays	Sc/clays	Cs/clays	Co/clays
Mean	0.23	0.12	0.38	0.30	0.43
SD	0.046	0.025	0.091	0.033	0.070
% (SD/mean)	20	21	24	11	16

were considered (Table 4). One can note that among the 10 cores analysed by the latter author, only three were long enough to reach the background levels, according to the local sedimentation rates (Zuo et al., 1991; Radako-vitch, 1995) and the indicated lead contamination in local sediment cores (Ferrand et al., 1999).

For most metals, and most of the reference values, the metal/Cs ratios are quite similar, indicating that our method is suitable for the detection of the natural background values. Only in the shale of Krauskopf (1967), the ratios are systematically higher than both in the other reference values, and in most of our non-polluted samples. This shale has probably an out-standing position and we therefore refer mainly to the other literature reference values in Table 4. One can notice that also the local pre-anthropogenic sediment values are in good agreement with both our values and the other reference ratios.

The good agreement of the natural metal/Cs ratios from the literature with our samples is especially true for Co, Cr, Cu and Ni. Nevertheless, the higher Ni/Cs ratio observed in local pre-anthropogenic sediments is much more difficult to explain. But it is interesting to note that a similar shift between our surficial sediment samples and those of Marin (1998) is observed, suggesting the influence of the analytical procedure. On the other hand, our ratios are more elevated for Pb and Zn.

The too elevated value for lead is interesting in this context because it seems to reflect the impact of aerosol deposition in the Gulf of Lions. It is well known that this trace metal has contaminated the troposphere, mostly during the 19th century by human activities related to gasoline combustion and metal processing (Nriagu and Pacyna, 1988). Associated with submicron particles, the pollutant can be advected over long distances and reach remote terrestrial and marine environments (Hernandez et al., 2003; Settle and Patterson, 1982). The situation in the study area is quite complex since both anthropogenic and natural sources of aerosols are mixed in the sediment (Grousset et al., 1994). But these different origins can be traced by their isotopic signatures (Véron et al., 1992), and the anthropogenic contribution in the overall lead concen-trations can therefore be estimated.

Among the four stable isotopes of lead (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb), the ^{206}Pb/^{207}Pb ratio is the most commonly used for the detection of anthropogenic sources because of its generally low standard deviation and its insensitivity to mineralogical changes in the sediments. In this work, lead isotope analyses have been performed on a subset of 17 surficial sediment samples spreading over the entire continental margin (see Fig. 1, Table 5). We focused our attention on both ratios. When plotting our data in a ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb diagram (Fig. 5), they globally fall on the mixing line of the main end-members given by the literature: local pre-

Table 5
Lead isotope ratios and inverse lead concentrations of some surficial sediments of the Gulf of Lions ($n=17$)

Stations	Longitude	Latitude	206/204	206/207	1/Pb
08	4.638	42.822	18.435	1.176	0.022
09	4.403	43.442	18.408	1.185	0.018
09X	4.832	43.233	18.319	1.184	0.023
12	4.591	42.978	18.319	1.182	0.021
16	4.086	43.217	18.526	1.182	0.024
21bis	3.534	43.226	18.52	1.188	0.038
25	3.848	43.048	18.46	1.183	0.022
26	3.97	42.851	18.384	1.177	0.025
29bis	3.45	42.91	18.526	1.184	0.024
35	3.065	42.716	18.771	1.198	0.035
38bis	3.439	42.542	18.523	1.177	0.023
39bis	3.511	42.449	18.26	1.176	0.024
CH20	4.854	43.314	18.628	1.181	0.022
KB4	4.868	43.318	18.588	1.184	0.021
KB16	4.824	43.32	18.548	1.186	0.022
PL1	5.221	43.095	18.346	1.177	0.019
PL2	5.192	43.021	18.32	1.180	0.016

anthropogenic sediments (Ferrand et al., 1999), leaded gasoline (Monna et al., 1997) and some commonly used industrial aerosol signatures (Monna et al., 1997; Véron et al., 1999). Only station 35 (Table 5) presents outstanding ratios, falling in the range of the local pre-anthropogenic levels, which rarely occurs in modern surficial sediments, except after the rapid deposition of Saharan aerosols. But the corresponding Pb/Cs ratio, which is similar to those of the entire study area, does not support such a hypothesis. Station 35 refers to the Têt river mouth, in the western part of the Gulf of Lions (Fig. 1). Camarero et al. (1998) defined the lead isotopic ratios of pre-anthropogenic sediments in Pyrenean lakes, which can be used as local background reference for the Têt river basin. The latter author found significantly
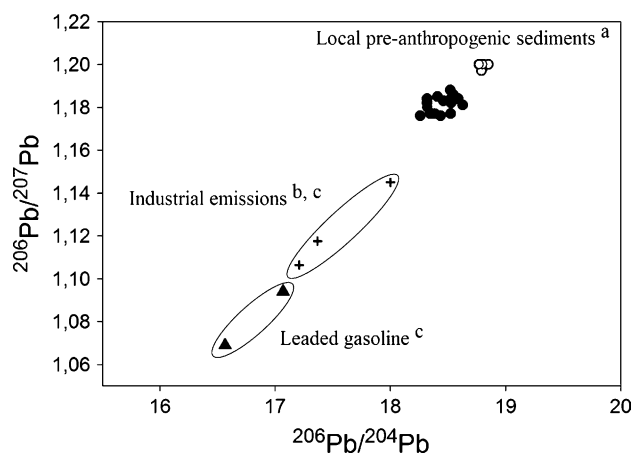

Fig. 5. Lead isotopic composition of surficial sediments of the Gulf of Lions ($n=17$, black circles). The main end-members are also represented in this diagram. [a]Ferrand et al. (1999), [b]Véron et al. (1999), [c]Monna et al. (1997).

more radiogenic values than those of Ferrand et al. (1999). It is therefore possible that the suspended river material discharged by this river may have a different natural lead isotopic signature compared to the general trend observed in the Gulf of Lions. As a consequence, we estimated the anthropogenic lead contribution in this station differently compared to the other stations (see below).

When looking at Fig. 5, it becomes evident that our surficial samples received an anthropogenic lead contribution, distinguishing them clearly from the local natural levels, even if the degree of contamination is more difficult to determine according to the wide range of anthropogenic signatures revealed by the literature. To do so, we plotted in Fig. 6 the $^{206}Pb/^{207}Pb$ ratio versus the inverse of the lead concentration of our data, including also the data for local anthropogenic levels determined by Ferrand et al. (1999). The corresponding regression results in a high correlation coefficient ($r^2=0.82$, $n=22$) and an intercept of 1.170 ± 0.009, giving the mean anthropogenic signature of the $^{206}Pb/^{207}Pb$ ratio. The distance of some data points from the regression line is probably due to the complex mixing of the different anthropogenic lead sources that affect the entire study area heterogeneously, identifying several geographic units (see Fig. 6). Thus, the mean anthropogenic signature can only be considered as a global estimation.

Following the same procedure, the mean anthropogenic $^{206}Pb/^{204}Pb$ ratio can be estimated to be about 18.220 ± 0.22 ($r^2=0.73$, $n=22$). Therefore, our mean anthropogenic ratios clearly fall outside of the range of the gasoline isotopic compositions, which are less radiogenic (according to Monna et al. (1997), $^{206}Pb/^{207}Pb=1.069-1.094$ and $^{206}Pb/^{204}Pb=16.564-17.068$). This indicates that industrial emissions are mainly responsible for the anthropogenic lead input to the Gulf of Lions, even if a mixture of the different end-members is possible. These results correlate well with the trend observed in recent studies, revealing an increase of the anthropogenic radiogenicity (Flament et al., 2002; Véron et al., 1999; Ferrand et al., 1999). This shift seems to be principally due to the diminution of the automotive lead impact since the use of unleaded gasoline.

Based on the $^{206}Pb/^{207}Pb$ ratio, which is considered as an independent index, an estimation of the aerosol contribution to the total lead concentrations is possible, using the following mixing equation:

Anthropogenic contribution (%)

$$= \frac{\left(^{206}Pb/^{207}Pb\right)_{sample} - \left(^{206}Pb/^{207}Pb\right)_{natural}}{\left(^{206}Pb/^{207}Pb\right)_{anthropogenic} - \left(^{206}Pb/^{207}Pb\right)_{natural}} \times 100$$

However, due to the different pollution sources that can contribute to the anthropogenic signatures, the plot distribution requires a correction in order to avoid misleading results. We therefore decided for the data points that obviously withdraw from the regression line in Fig. 6, to project them orthogonally to the regression line in order to recalculate the corresponding
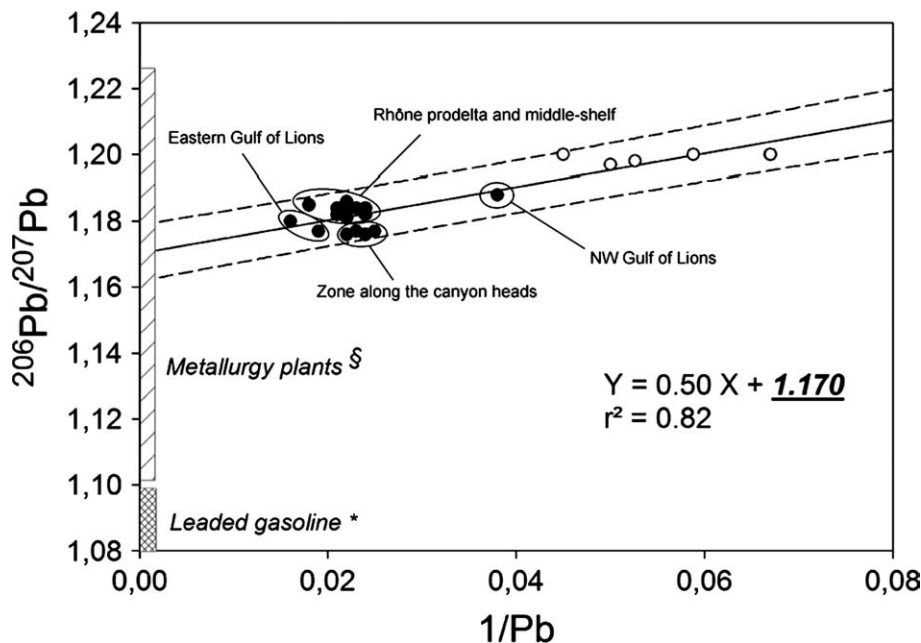

Fig. 6. Diagram of $^{206}Pb/^{207}Pb$ ratios versus inverse of lead concentrations in surficial sediments (black circles). Some local pre-anthropogenic values have been added to the linear regression (data from Ferrand et al. (1999), open circles). Isotopic signatures of both metallurgy plants and gasoline are presented by straight lines. §Véron et al. (1999), *Monna et al. (1997).

^{206}Pb/^{207}Pb ratios. The natural signatures have been averaged and station 35 has been processed with the natural values of Camarero et al. (1998).

As a result, the overall anthropogenic lead contribution to the Gulf of Lions can be calculated to range between 36 and 71%, with a mean value of 61%. This is in accordance with the results of local investigations (Ferrand et al., 1999) and recent works on some French forest soils (Hernandez et al., 2003). In general terms, the contamination seems to be uniformly spread over the study area, except for a low value observed in the NW part of the Gulf (Fig. 6) and the stations in the eastern part which reveal the highest contributions, probably due to the impact of the nearby city of Marseille. It is interesting to note that the influence of the Rhône, Petit-Rhône and Têt (not shown) rivers on the lead input (recorded in the corresponding prodeltas) seem to be of the same magnitude as those in the offshore stations. This indicates that aerosols deposited in the river basins are progressively eroded and river-transported to the marine environments, where they meet the aerosol inputs coming from direct deposits on the sea–atmosphere interface. Both fluxes are finally mixed and spread over the entire margin by local hydrodynamics and sedimentary processes.

These results allow us now to estimate the background signature for lead on the basis of our samples that were corrected for the atmospheric contribution. The normalization of the resulting "natural" Pb by Cs gives the value of 2.20, which is about half the previously calculated value (Table 4). This ratio is now in very good agreement with most of the ratios in our reference literature values, and more precisely the local pre-anthropogenic sediment of Marin (1998).

For Zn, the slight enhancement of the Cs normalized background value compared to the literature data is more difficult to explain. It is possible that in the Gulf of Lions, the natural Zn levels are greater than in the reference shale of Taylor and McLennan (1985), but the deepest samples of local sediment cores of Marin (1998) suggest that our value might be slightly affected by anthropogenic sources. The other possibility is that, like in the case of Pb, also for Zn, pollution is more widespread in the Gulf of Lions and affects the sites offshore the river deltas. It is generally admitted that Zn in aerosols of the NW Mediterranean is essentially of anthropogenic origin (Löye-Pilot, personal communication), which means that this element may also be widely introduced into the platform via the two pathways (i.e. direct deposit and river transport) described previously. Note that a similar enhancement was observed using the other normalizers, underscoring the trend of a slight anthropogenic influence for Zn in the entire study area. Further work is needed to confirm and/or to reject this hypothesis. Nevertheless, we consider that the local pre-anthropogenic sediment values calculated from Marin

(1998) may probably be the best estimate for the natural background values in the Gulf of Lions.

4. Conclusions

The purpose of this study was to test the ability of different potential normalizer elements to detect the degree of heavy metal pollution in surface sediments of the Gulf of Lions. Among the different candidates for normalization we tested, Cs appeared to be the most appropriate choice when compared to Al, Fe and Sc, the most currently used normalizer elements. It better reflected the fine-grained sediment and was the least sensitive to the silt fraction in our study area. The normalization capacity of this element has probably been overlooked in previous studies, although this has naturally to be confirmed by additional studies in different environments.

Using this element in the fraction <63 μm, we obtained, with a high confidence level, the local background signal of Co, Cr, Cu, Ni and Pb. This is confirmed both by comparing them to other literature values for non-polluted areas and to local pre-anthropogenic sediments. For lead, however, the aerosol contribution to the overall concentrations has to be estimated and removed first, because of the major influence of the atmospheric particles on the total lead concentrations in the surficial sediments. Directly deposited on the sea–atmosphere interface or river-transported with terrestrial particles, these man-made aerosols may be subsequently spread over the entire platform by hydrodynamics and/or sediment resuspension. Also for Zn, it is possible that the atmospheric deposition plays an important role in the introduction of this element in the marine environment, since the normalized Zn values also revealed a slight enrichment compared to local pre-anthropogenic sediment. But the data do not allow further confirmation or rejection of this hypothesis.

Except Zn, for which the deep sediment core signal may be preferred, our results indicate that the backgrounds obtained can be used as the most appropriate references for further regional studies on the heavy metal pollution in the Gulf of Lions and/or similar regions. The appropriate background level choice is crucial for the interpretation of the pollution state in the coastal environment. Non-representative of regional specificities, literature references may yield conflicting conclusions on the cause of enhanced metal levels (i.e. anthropogenic enrichment or natural variability), as suggested by other authors (Rubio et al., 2000; Gibbs, 1993). Of course, in the case of our samples, one should mention that also the selection of most of the other normalizer elements allow general distinction between the polluted and non-polluted areas in the Gulf of Lions, since the correlations with the fine-grained

fractions in the sediments are still reasonably good. However, the resulting pictures are much less detailed, and some important information can be lost in the interpretation of the general distribution patterns.

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